

Cryptic chemical identification as a crime intelligence aid

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A dead body was found near the sea and a commercial port in north-east Italy. The man had been shot and then burnt, by using a large volume of fire accelerant. The chemical composition of the flammable mixture had to be determined in order to aid police investigations. GC-MS analysis of residual cloth and soil identified a common gasoline, together with some unrelated compounds deriving from the container used to carry the inflammable liquid. A reconstruction of the event, an examination of the surroundings where the crime took place and the cryptic chemicals found, enabled the investigators to restrict and intensify their enquiries within a specific area.

Un cadavre a été découvert près de la mer et d'un port commercial du nord-est de l'Italie. L'homme avait été tué par balle puis brûlé en utilisant un grand volume de combustible accélérateur de feu. La composition chimique du mélange inflammable a dû être déterminée pour aider la police dans son enquête. Une analyse par GC-MS du reste des vêtements et du sol ont permis d'identifier une benzine commune, ainsi que des composés indépendants provenant du conteneur utilisé pour transporter le liquide inflammable. Une reconstruction de l'évènement, un examen des environs d'où le crime avait eu lieu et des produits chimiques cryptiques trouvés, ont permis aux enquêteurs de restreindre et d'intensifier les recherches dans une zone spécifique limitée.

An der Küste Nordostitaliens wurde in einem Feld in der Nähe eines Handelshafens die Leiche eines Mannes aufgefunden. Der Mann war erschossen und mit einer großen Menge Brandbeschleuniger verbrannt worden. Zur Unterstützung der polizeilichen Ermittlungen sollte die chemische Zusammensetzung des Brandlegungsmittels bestimmt werden. Die GC-MS Analyse an Kleidungsresten und Bodenproben ergab den Nachweis eines weitverbreiteten Kraftstoffs und einiger Fremdbestandteile, die vom Transportbehälter für das Brandlegungsmittel stammten. Eine Rekonstruktion des Geschehens, die Untersuchung des Tatortes und die gefundenen Fremdbestandteile ermöglichten den Ermittlern ihre Nachforschungen auf ein bestimmtes Gebiet einzuschränken und zu konzentrieren.

Se encontró un cadáver cerca del mar, en un puerto comercial del Noreste de Italia. El hombre había sufrido un disparo y luego había sido quemado usando gran cantidad de acelerante de fuego. El análisis GC-MS de los restos de ropa y suelo, identificó gasolina común junto con algunos compuestos no relacionados que procedían del contenedor utilizado para transportar el líquido inflamable. La reconstrucción del suceso, el examen de los alrededores del crimen y los productos químicos encontrados, permitió a los investigadores restringir e intensificar sus pesquisas dentro de un área específica.

Key Words: Forensic science; Crime scene examination; Gas chromatography; Dichlorotoluenes; Mass spectrometry; Thermal desorption cold trap injection.

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Introduction

High performance analytical chemistry techniques may provide a fundamental contribution to the resolution of many complex cases in forensic science [1–7]. Chemical analysis, together with other investigative procedures, may sometimes interpret a crime scene, which would otherwise appear difficult to reconstruct.

The most appropriate technique to detect chemical compounds at low concentrations in complex matrices is high resolution gas chromatography coupled to mass spectrometry (HRGC-MS). This technique can identify chemical compounds of interest even if co-eluting with other components. High sensitivity is a typical advantage of this technique, but it can be further increased by on-line sample extraction, trapping and injection of the analytes [7–8].

In a recent case, the chemical composition of a flammable mixture was required in order to facilitate police investigations. A dead body had been found in a field by the sea and not too far from a commercial port in the north-east of Italy. The man had been shot and then burnt, by spreading and then igniting a large volume of fire accelerant on his body. The crime had taken place at the end of December, during the night. The body was found in the morning; the weather was icy, with a temperature largely below 0°C. Sampling was carried out twenty-four hours after discovery.

This paper reports the data obtained by GC-MS analysis of residual cloth and soil samples, which identified the accelerant, together with some unrelated compounds originating from the container used to carry the flammable liquid. Further investigation of these compounds was able to narrow the area of investigation of the crime.

Preliminary investigation

Experimental

Soil samples and unburned clothes including a pile jacket, trousers, socks and a shirt, which had been collected from around and under the dead man's body, were submitted for chemical investigation. The soil and cloth samples were dried under calcium chloride in a Petri box, to eliminate moisture which could interfere during the analysis. Dried samples were submitted successively to one of two extraction processes.

On-line extraction used a thermal desorption cold trap injector Chrompack 4010, coupled to a GC-MS system. The analyte extraction was obtained by thermal stripping at 180°C for 5 min, simultaneous cryogenic trapping at -100°C and successive flash injection at 250°C, directly into the chromatographic column, for GC-MS analysis.

Off-line treatment comprised solvent extraction of dried materials. After dichloromethane extraction for 10 min under ultrasonic action, one microlitre of organic phase was injected into the chromatographic column for analysis.

All the measurements were performed using a Hewlett-Packard GC-MS system which consisted of a HP 5890 gas chromatograph coupled to a HP 5971A mass detector. The chromatographic separations were obtained, by analyte elution from each sample, through a capillary column HP 50+ (diphenyl-50%/dimethylpolysiloxane-50%) having the following dimensions: length, 30 m; internal diameter, 0.25 mm and film thickness, 0.5 µm. The chromatographic conditions for all the GC-MS runs were: Temperature program; 50°C x 1 min – 10°C/min – 220°C x 20 min and transferline at 280°C. The mass detector, in the Scan mode, detected the ions generated by electron ionisation (70 eV) at a 176°C ion source temperature, within the mass recording window from 50 to 280 Dalton.

Results

Under the same experimental conditions, the analytical response showed a high precision for replicate analyses.

Some soil samples, submitted to thermal desorption treatment followed by GC-MS analysis, showed the presence of light aromatic hydrocarbons (C1–C4 alkylbenzenes), phenols, and polycyclic aromatic hydrocarbons ranging from naphthalene to pyrene, including various higher homologues such as methyl- and/or dimethyl-substituted compounds. Moreover, high concentrations of five DCT isomers were detected. The same light aromatic hydrocarbons, phenols, polycyclic aromatic hydrocarbons and DCT were found in the clothes, mostly on the pile jacket.

Dichlorotoluene (DCT), and the fire accelerant components were identified by comparing the GC-MS responses of the samples with their respective standards. DCT commercial isomers, such as 2,4-, 2,5-, 2,6- 3,4- and 2,3- were purchased from Aldrich-Chimica, Milan, Italy.

Trichlorotoluene (TCT) detection was performed in a selected ion monitoring mode, recording the specific ions at m/z 159 and 196 Dalton.

Further investigation

Analysis of the soil and cloth samples thus highlighted four significant classes of compound.

As regards light aromatic hydrocarbons, the extracted chromatograms of diagnostic ions, such as m/z 91, 105 and 119 for toluene, xylenes, C3- and C4-alkylbenzenes when compared with those obtained from commercial fuels, classified the found mixture as gasoline. Target-compounds (C1–C4 alkylbenzenes) were diagnostic for any trademark gasoline. The presence of polycyclic aromatic hydrocarbons may be attributed to heavy mineral oil or organic material combustion. Their detection on jacket parts, which were unburned and not contaminated by soot, meant that these compounds did not derive from cloth combustion. Consequently, they had to be linked to an unintentional introduction into the crime scene.

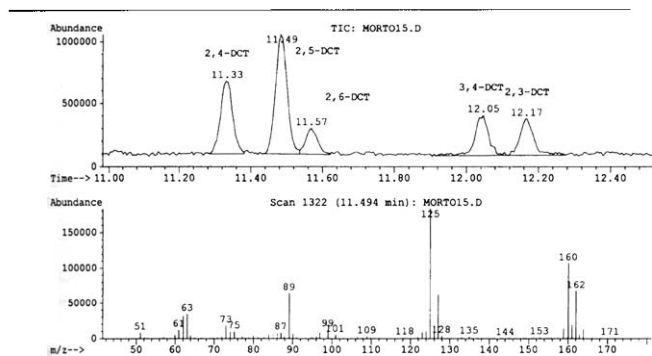


FIGURE 1 Chromatogram and mass spectrum of DCT found in cloth and soil samples.

The presence of phenol and some of its alkyl-derivatives, such as cresols and dimethylphenol, was difficult to interpret due to the lack of evident parent-materials [9]. The finding of the same compounds in an examined commercial formulation allowed clarification of their origin.

The finding of halogenated compounds in the forensic samples was unusual. The specific isomers were identified and determined as a result of the GC-MS responses of the authentic standards (Figure 1).

DCT mixtures

The chemical and physical properties of DCT mixtures suggest that DCT cannot be used as a fuel additive, considering its high flash point and because burning may produce HCl which corrodes engines. In fact, no trace of these compounds was found in the analysed trademarked gasoline and diesel additives [10].

Polyester thermoxidation and pyrolysis do not produce DCT. PVC can generate it, but the analysed samples lacked most of the halogenated species, such as di- and trichlorobenzenes [9], obtained in this way.

One possible use for these compounds could be as a carrier in the fabric dyeing process, but considering the high concentrations detected in both samples, the pile jacket and soil, this can be ruled out. In any case, pile samples from other derivations, under the same analysis conditions, showed no trace of these solvents [11].

DCT is non-flammable, but combustible, and is not, therefore, particularly effective as a fire accelerant [10].

The DCT synthesis process leads to by-product isomers of limited industrial value. Some of its isomers are important as intermediates for key product synthesis in the pharmaceutical and agricultural field [11], but DCT synthesis, starting from chlorotoluene, is not selective, so that the result is an isomer mixture [11]. This almost worthless isomeric fraction, separated by distillation, makes up the common technical solvent for unspecific use. Its composition varies, depending on the starting reagent (o- and/or p-chlorotoluene), chlorination and distillation conditions. Uses of

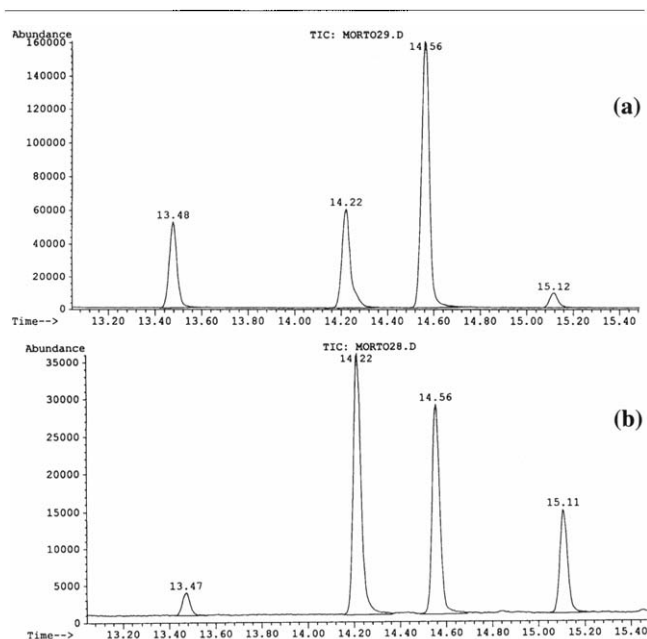


FIGURE 2 Chromatogram of TCT detected in (a) DCT from company A and (b) cloth samples.

unspecific DCT mixture include trading formulations for a carbon remover solvent cleaner, a grease remover solvent cleaner, a quick separating degreaser, a microemulsion solvent cleaner for engine carburettors and a carrier and/or solvent for dyes.

In Italy, at the time of writing, three companies, in this paper named as A, B and C, produced and/or sold, pure DCT, mixtures and trade formulations. The commercial formulation of samples containing DCT and the relative safety sheets were furnished by the respective manufacturers. All the DCT mixtures and carbon removers present on the Italian market were analysed, in order to verify which company made or sold the DCT mixture found at the crime scene.

Company A

Its commercial carbon remover, utilised in the naval field, contained DCT which showed a very different GC-MS chromatographic pattern. Moreover, this DCT mixture was always linked to the presence of about 10% monochlorotoluenes, added to avoid solidification at low temperatures. This monosubstituted toluene was not detected in the soil and cloth samples.

The GC-MS analysis of trichlorotoluenes (TCT), by-products of the chlorination reaction, gave a chromatographic profile that could not be superimposed on the one obtained for the unknown samples (Figure 2). Consequently, it was concluded that the DCT and its formulations produced by this company were unrelated to the case under investigation.

Company B

GC-MS analysis of the DCT mixture by this company

showed many analytical responses that were similar to those detected for the original samples. All the DCT isomers were present with slight differences in amount. Monochlorotoluenes were absent and TCT chromatogram was perfectly superimposable. However, this specific DCT mixture was used only in a minor textile sector operating in a limited area, hundreds of kilometres away from the crime scene. These considerations ruled out the DCT produced by B from further investigations.

Company C

Products by C were used to clean engines or metallic parts in the naval field only. On GC-MS analysis of a carbon remover, the DCT (Figure 3) and TCT (Figure 4) chromatographic fingerprints were found to be very similar to those from the original samples (Figures 1 and 2b respectively). In this formulation, phenol, cresols and dimethylphenol were present (Figure 5a) and corresponded also to the data obtained from the jacket sample (Figure 5b). The retention time differences were due to the different injection mode: usual GC injector and thermal desorption cold trap injector, respectively. The chromatographic conditions were equivalent and peak identification was carried out by mass spectra. No monochlorotoluene traces were found in this commercial product. These results led to the conclusion that the product manufactured by C was implicated in the examined case.

Conclusions

Summarising the analysis results, the information and documentation acquired, it was possible to depict a possible crime scenario. The fire accelerant used in the criminal event was gasoline fuel. The gasoline was carried to the crime site using a container where at least a small quantity of detected DCT mixture was present.

Halogenated compounds, which contaminated the gasoline, were carbon remover components produced under the trademark of company C. In fact, the solvent cleaner examined showed a strong DCT correspondence in chromatographic pattern (five isomers), as well as TCT (four isomers) and phenolic species (four homologues) with those detected from the original samples.

The presence of polycyclic aromatic hydrocarbons (PAH) would suggest that the carbon remover held in the container was not fresh, but had already been used to clean something, such as an engine.

The reconstruction of the event, the surroundings where the crime took place and the aid of the chemicals found, persuaded the State Prosecutor to restrict and intensify his enquiries only to the maritime and naval sector. The resulting contribution was considerable. In fact, without it the only thing that was clear was that gasoline had been used and no further information was available to direct the investigators' enquiry towards a specific area.

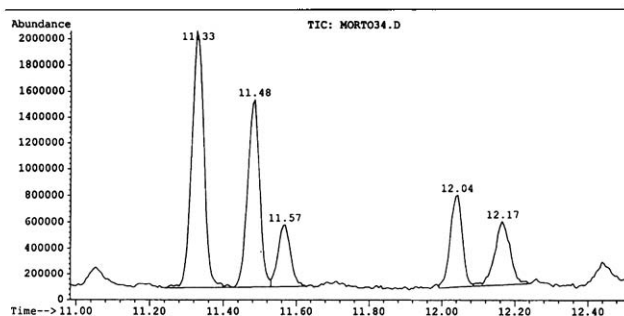


FIGURE 3 Chromatogram of DCT from company C.

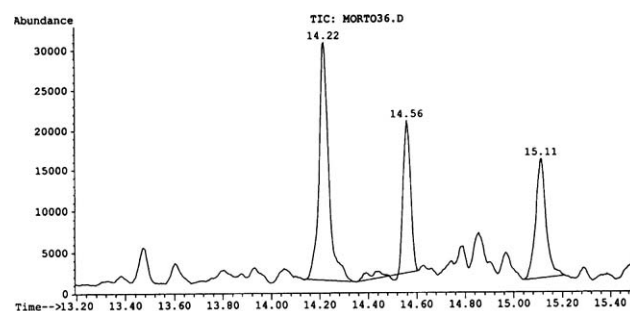


FIGURE 4 Chromatogram of TCT detected in DCT from company C.

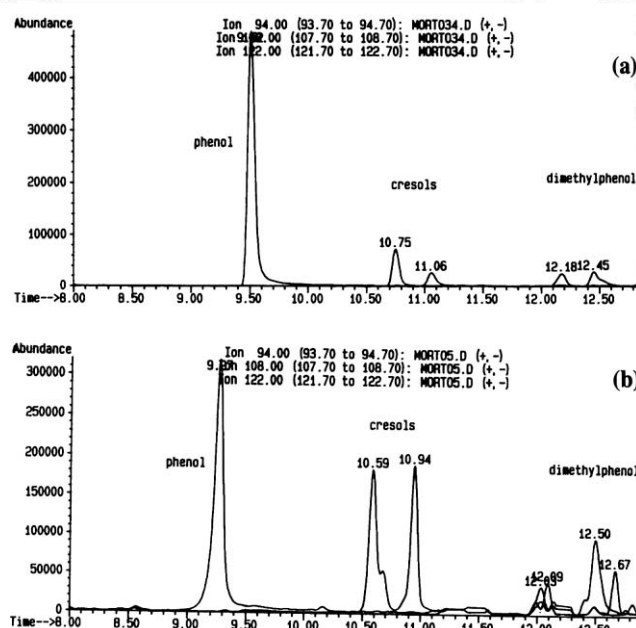


FIGURE 5 Phenolic species detected in (a) carbon remover from company C and (b) victim's clothes.

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References

1. Lennard CJ, Tristan Rochaix V, Margot P, Huber K. A GC-MS database of target compound chromatograms for the identification of arson accelerants. *Science & Justice* 1995; 35(1): 19–30.
2. Keto RO. GC-MS data interpretation for petroleum distillate identification in contaminated arson debris. *Journal of Forensic Sciences* 1995; 40(3): 412–423.

3. Coulombe R. Chemical markers in weathered gasoline. *Journal of Forensic Sciences* 1995; 40(5): 867–873.
4. Schuberth J. Post mortem test for low boiling arson residues of gasoline by gas chromatography ion trap mass spectrometry. *Journal of Chromatography B, Biomedical Applications* 1994; 662(1): 113–117.
5. Ojampere I, Hyppola R, Vuori E. Identification of volatile organic compounds in blood by purge and trap plot capillary gas chromatography coupled with Fourier transform infrared spectroscopy. *Forensic Science International* 1996; 80(3): 201–209.
6. Dhole VR, Ghosal GK. Detection and characterization of petroleum based accelerants in fire debris by HPLC. *Journal of Liquid Chromatography* 1995; 18(9): 1767–1786.
7. Jackowski JP. The incidence of ignitable liquid residues in fire debris as determined by a sensitive and comprehensive analytical scheme. *Journal of Forensic Sciences* 1997; 42(5): 828–832.
8. Goosens EC, De Jong D, De Jong GJ and Brinkman UATH. On-line sample treatment – Capillary gas chromatography. *Chromatographia* 1998; 47(5/6): 313–345.
9. Levin BC. A summary of the NBS literature reviews on the chemical nature and toxicity of the pyrolysis and combustion products from seven plastics: acrylonitrile-butadiene-styrenes (ABS), Nylons, polyesters, polyethylenes, polystyrenes, poly(vinyl chlorides) and rigid polyurethane foams. *Fire and Materials* 1987; 11: 143–157.
10. Sigma-Aldrich-Fluka. The MSDS Material Safety Data Sheets. Milwaukee, WI, 1996.
11. Grayson M, Eckroth D, editors. *Kirk-Othmer Encyclopedia of Chemical Technology*. New York: Wiley & Sons, 1984; 5: 823–825.